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14. ABSTRACT A simple sputter source of thermal silicon carbide cluster anions has been developed and tested. Vibrationally resolved photoelectron spectra have been obtained for a number of anions of the form $Si_nC_m^-$ , with $n+m \leq 8$ . Full interpretation of the spectra requires accurate calculation of the anion structure, carried out in collaboration with Gordon (ISU) and Burggraf (AFIT). The first fully analyzed spectra and calculations for asymmetric species ( $n < m$ ) are complete; two three manuscripts describe this work. A laser ablation ion source has been designed to produce the important (but difficult to produce) $n=m$ $Si_nC_m^-$ ions. Other new work systematically investigates the complex electronic structure of the nickel column metal oxides.					
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# AFOSR Final Report

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## Photoelectron Spectroscopy and Dynamics of Adsorbates on Clusters

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### Objectives

We utilize anion photoelectron spectroscopy to obtain electron affinities and information on low lying excited states of small silicon carbide clusters, and on similar clusters possessing a single oxygen adatom. The initial emphasis was placed on the smallest clusters, providing a quantitative basis for comparisons with *ab initio* calculations carried out by Professors L. Burggraf and David Weeks (AFIT) and Mark Gordon (ISU). These data provide important benchmarks to evaluate and guide development of theoretical approaches to modeling surface chemistry using a cluster-in-a-continuum approach, such as SIMOMM. A particularly important aspect of these theoretical and experimental studies is the emphasis on **both** ground and excited state properties of these clusters. Very little is known at present concerning excited states, the calculation of excited state properties is a major challenge to theory, and yet these states surely play important roles in the adsorbate surface chemistry.

### Accomplishments

This report summarizes our activities over the period from May 1, 1999 through February 28, 2002. This has been a collaborative experimental/theoretical project with the first objective to obtain experimental data, the second to obtain accurate *ab initio* anion and neutral cluster structure calculations and the third to carry out dynamical simulations on the surfaces. We have continued to make steady progress in the first two areas and have plans to carry out molecular dynamics simulations in the future. Progress in each of the experimental areas is briefly summarized in the following sections:

## Experimental

The very simple silicon carbide cluster ion source continues to be an extremely useful device. We are able to produce usable quantities of a substantial variety of small silicon carbide clusters containing up to about eight atoms. Figure 1 is a typical mass spectrum from the ion source and gives a feeling for the kinds of ions that can be produced. In addition, we have learned that the C/Si composition of the ions in the mass spectrum can be changed by changing the temperature of the He buffer gas. This result is not understood well but it obviously reflects the temperature dependence of the clustering reactions, rather than the sputter process itself.

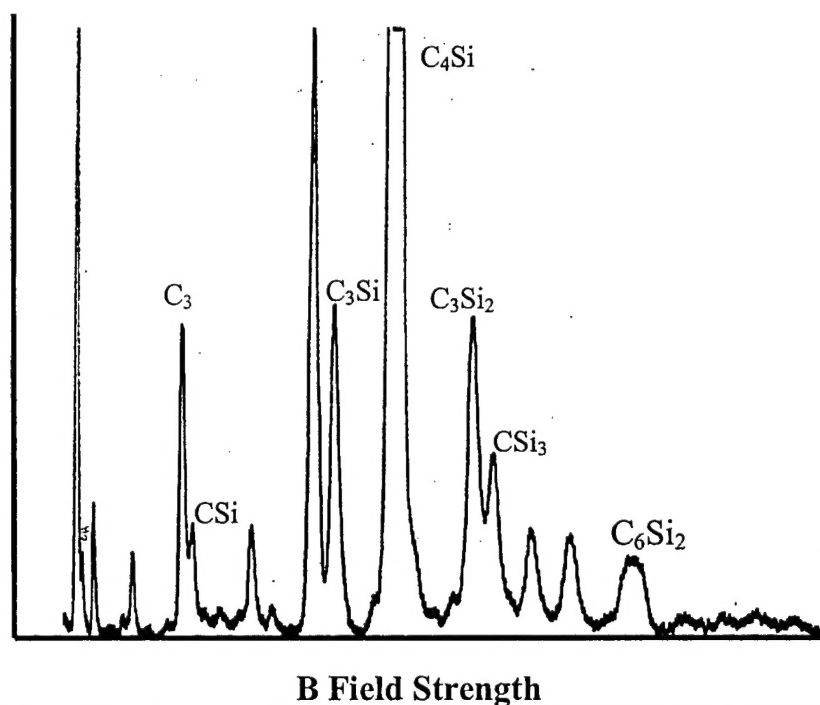


Figure 1. Mass Spectrum of Anions Sputtered from a SiC Rod.

The long-term goal of all of the experiments is to study the properties of adsorbates on these clusters, particularly oxygen, atoms and molecules. While the intensity of the cluster ion beams is marginally adequate for photoelectron spectra, obtaining such data has presented a substantial challenge and emphasized the need to improve the sensitivity of the photoelectron spectrometer. This improvement in sensitivity was carried out by installing a new position

sensitive detector with higher spatial resolution, allowing operation of the photoelectron energy analyzer at higher transmission energy. The higher transmission energy translates directly into a broader collection energy window and correspondingly improved efficiency. The new detector has provided about a factor of five improvement in efficiency, without a significant loss in energy resolution.

## Experimental Results

While we have obtained data on a number of cluster ions, quantitative interpretation of the data have awaited sophisticated electronic structure calculations on both the anion and the neutral. Without such calculations, the interpretations are somewhat limited. The first clusters for which such calculations are available to extend the experimental interpretations are for the

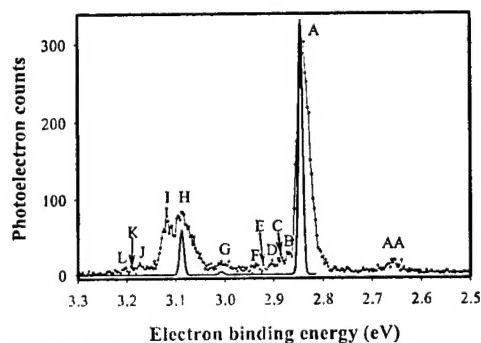


Figure 2.  $\text{C}_3\text{Si}^-$  364 nm Photoelectron Spectrum.

$\text{C}_3\text{Si}$  and  $\text{C}_4\text{Si}_2$  anions. Electronic structure calculations by our group and more sophisticated calculations from the Gordon group now allow an unequivocal analysis. For example, the photoelectron spectrum of  $\text{C}_3\text{Si}^-$  is shown in Figure 2.<sup>1</sup> A detailed analysis gives the electron affinity,  $2.827 \pm 0.007$  eV, and information on the term energy of the first ( $^1\Delta$  or  $^1\Sigma$ ) electronically excited state of  $\text{C}_3\text{Si}$ .

The latter identification depended heavily upon the elaborate calculations<sup>2</sup> carried out in our collaboration with the Gordon group. In collaboration with Burggraf at AFIT, we are currently finishing a full analysis of the  $\text{C}_4\text{Si}^-$  photoelectron spectrum.

Similar experiments on  $\text{C}_4\text{Si}_2^-$  reveal a rather simple spectrum, shown in Figure 3. However, modeling of the spectrum does not allow assignment of all of the vibrations that are observed. The *ab initio* calculations carried out in our group indicated that there must be a second very low lying excited state, once again corresponding to either  $^1\Delta$  or  $^1\Sigma$ . The analysis gives the electron affinity as 2.543 eV and excitation energy of 0.110 eV. A fuller discussion of this analysis has been published.<sup>2</sup>

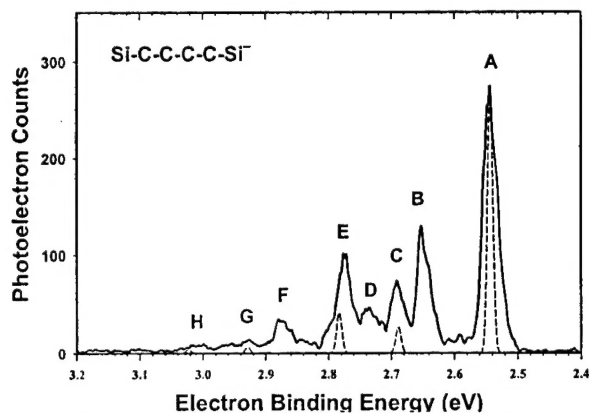


Figure 3.  $C_4Si_2^-$  364 nm Photoelectron Spectrum.

The odd total atom  $Si_nC_m$  species provide an especially challenging test experimentally and theoretically, as the anion is much more rigidly linear than the neutral. However, in either case, the bending vibrations are very low frequency and appear as sequence bands in the photoelectron spectrum. Thus, Figure 4 shows the photoelectron spectrum of  $Si_2C_3^-$ . All of the

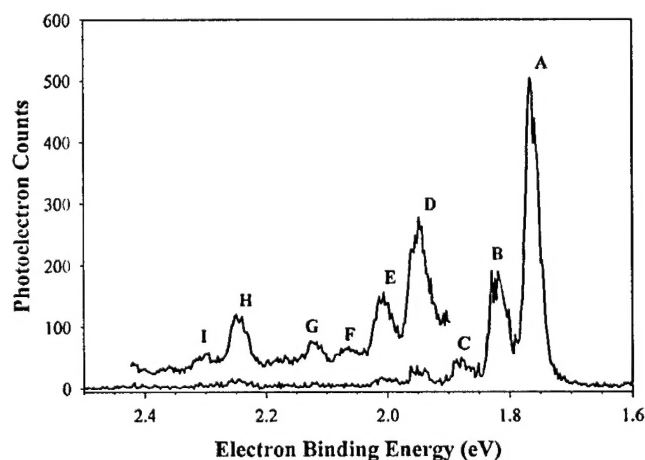


Figure 4.  $C_3Si_2^-$  364 nm Photoelectron Spectrum.

peaks show significant broadening as the ion source temperature is increased, a consequence of these low frequency bending modes. A full analysis has been completed in collaboration with Burggraf and Weeks, and the manuscript<sup>3</sup> has just been published.

Finally, AFOSR has partially supported a project that utilizes the same sputter ion source to investigate the low-lying electronic states of the nickel group oxides. The electronic states of these important oxides are extraordinarily complex as a result of open s- and d-shells, and the

almost complete failure of single configuration descriptions to give even a zero-order picture of the electronic states. We have made substantial progress in understanding the structure with the use of the spin-orbit coupling in the anions as a measure of electron localization on the oxygen atom. As one goes from NiO to PdO to PtO, the transition from ionic to covalent bonding is striking. A manuscript describing this work is in press.<sup>4</sup> Another brief study involved several undergraduate students and concerned the electronic structure of AgO.<sup>5</sup>

### **Personnel**

This grant partially supported the research of an outstanding Physics graduate student, Ms. Tanya Ramond. Dr. Ramond completed her PhD in August 2001, and accepted a prestigious NRC postdoctoral position with the ion storage group at NIST. Dr. Rebecca Schwartz was heavily involved as a postdoctoral associate until she accepted a position in the research laboratories of the FBI. Gustavo Davico was a postdoctoral associate, who departed JILA to become an Assistant Professor of Chemistry at the University of Idaho. Two relatively new PhD students, Mr. Django Andrews and Mr. Adam Gianola took over this project from Dr. Ramond.

### **Interactions/Transitions**

The work reported here was part of an ongoing collaboration with Professor Mark Gordon (Iowa State University) and Professors Larry Burggraf and David Weeks (Air Force Institute of Technology). The experimental work was focused at Colorado and the interpretations were guided by electronic structure calculations from ISU and AFIT. The interpretations will lead to time-domain studies that will be modeled using molecular dynamics simulations at AFIT. The investigators met regularly at Air Force Molecular Dynamics Contractors meetings, and further interactions are planned beyond this Grant.

### **Inventions and patent disclosures**

There have been no inventions leading to patent disclosures during the period of this grant.

### **Papers Published**

1. G. E. Davico, R. L. Schwartz, and W. C. Lineberger, "Photoelectron spectroscopy of C<sub>3</sub>Si and C<sub>4</sub>Si<sub>2</sub> anions," *J. Chem. Phys.* **115**, 1789-1794 (2001).
2. J. M. Rintelman and M. S. Gordon, "Structure and energetics of the silicon carbide clusters SiC<sub>3</sub> and Si<sub>2</sub>C<sub>2</sub>," *J. Chem. Phys.* **115**, 1795-1803 (2001).

3. X. F. Duan, L. W. Burggraf, D. E. Weeks, G. E. Davico, R. L. Schwartz, and W. C. Lineberger, "Photoelectron Spectroscopy of  $\text{Si}_2\text{C}_3^-$  and Quantum Chemistry of the Linear  $\text{Si}_2\text{C}_3$  Cluster and Its Isomers," *J. Chem. Phys.* **116**, 3601-11(2002).
4. T. M. Ramond, G. E. Davico, Fredrik Hellberg, F. Svedberg, P. Salén, P. Söderqvist, and W. C. Lineberger, "Photoelectron Spectroscopy of Nickel, Palladium, and Platinum Oxide Anions," *J. Mol. Spectrosc.*, in press.
5. D.H. Andrews, A.J. Gianola and W.C. Lineberger, "On the Photoelectron Spectrum of  $\text{AgO}^-$ ," *J. Chem Phys*, August 2002.